

Hexamethylenetetramine Mediated Simultaneous Nitrogen Doping and Reduction of Graphene Oxide for a Metal-Free SERS Substrate

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Experimental Details:

Graphene oxide (GO) was synthesized according to the modified Hummers' method. Then 50 mg of GO was taken in 50 ml of water solution in 100 ml of beaker and dispersed in the solution by ultrasonication for about 1 h. Then deep brown colour solution was collected by centrifugation remove the remaining black product. We used hexamethylenetetramine (HMT) and silver nitrate solution as source for N and Ag. All the experimental condition were written in the below table.

	Precursors			Reaction Time	Temperature
	GO solution	HMT	0.1M AgNO ₃		
N-rGO	10 ml (1mg/1 mL)	1 g in 10 ml	0 ml	10 h	180 °C
Ag(l)/N-rGO	10 ml (1mg/1 mL)	1 g in 10 ml	1 ml	10 h	180 °C
Ag(h)/N-rGO	10 ml (1mg/1 mL)	1 g in 10 ml	2 ml	10 h	180 °C

After the experiments, all the product was collected by centrifuges, washing with the DI water and ethanol several times. All the reaction was carried out in room temperature and ambient pressure. For synthesis of porous Pd/N-rGO nanostructures, we used Na₂PdCl₄ solution. We added 1 ml of 0.01 M of Na₂PdCl₄ solution in the dispersion of 1 ml of 250 µg of Ag(h)/N-rGO hybrid at room temperature and kept it for long time.

Characterizations:

The presence of Ag in the N-rGO was characterized by X-ray diffraction (XRD) using PANalytical X'Pert Pro equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). UV-visible spectra of all the sample was carried out on a Hitachi UV-vis spectrophotometer. The Raman scattering measurements of all the sample were performed on a Raman system (WITec) with confocal microscopy at room temperature. A Nd:YAG laser (532 nm) was used as an excitation source. The microstructures of the sample were characterized with field emission scanning electron microscopy (FE-SEM, FEI-INSPECTF50). Crystalline nature, shape and distribution of the Ag and porous Pd on N-rGO were characterized by transmission electron microscopy (TEM, JEOL- JEM-2100F) and high resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED)

pattern operated a 200kV accelerating voltage. The TEM sample was prepared by dispersing the sample in DMF solution by ultrasonic bath and drop casted on carbon coated copper grid, and then dried for TEM analysis. The X-ray photoelectron spectroscopy (XPS) was performed for the elemental analysis as well as the reduction of the functional groups of the GO and doping in the graphene. All the peak was deconvoluted using XPESPEAK41 software.

ESI-1

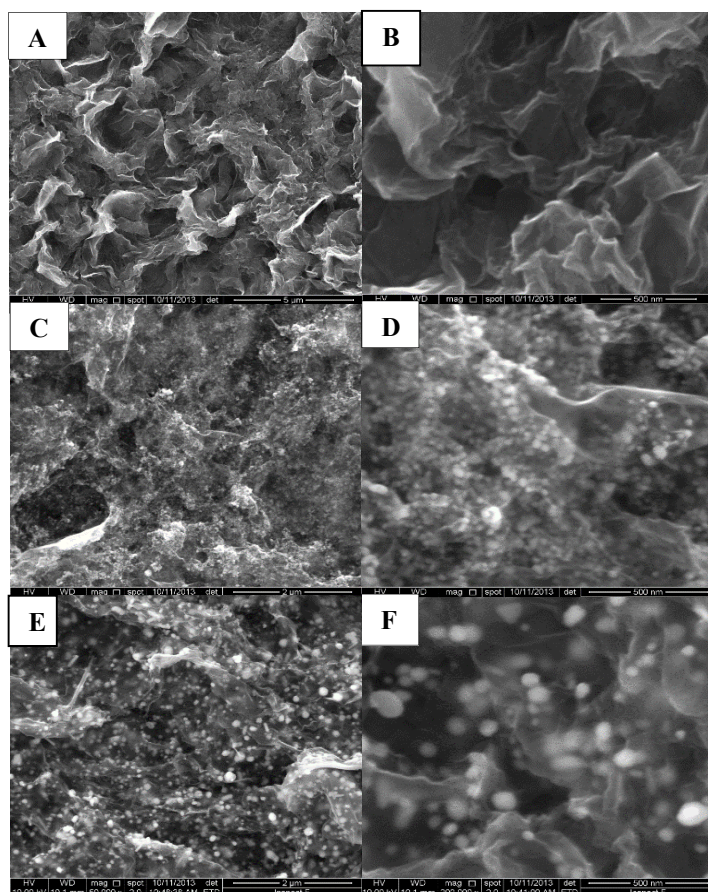


Fig. 1 SEM images of (A&B) N-rGO, (C & D) Ag(h)/N-rGO and (E &F) Ag(l) /N-rGO.

ESI-

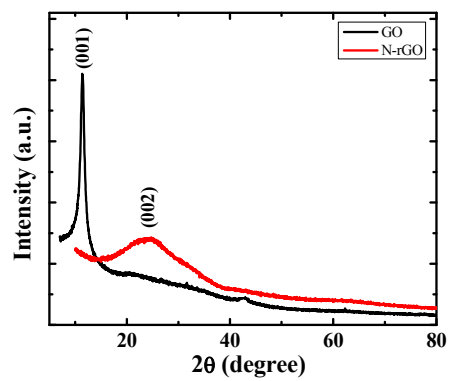


Fig 2. Powder XRD plot of GO and N-rGO.

ESI-3

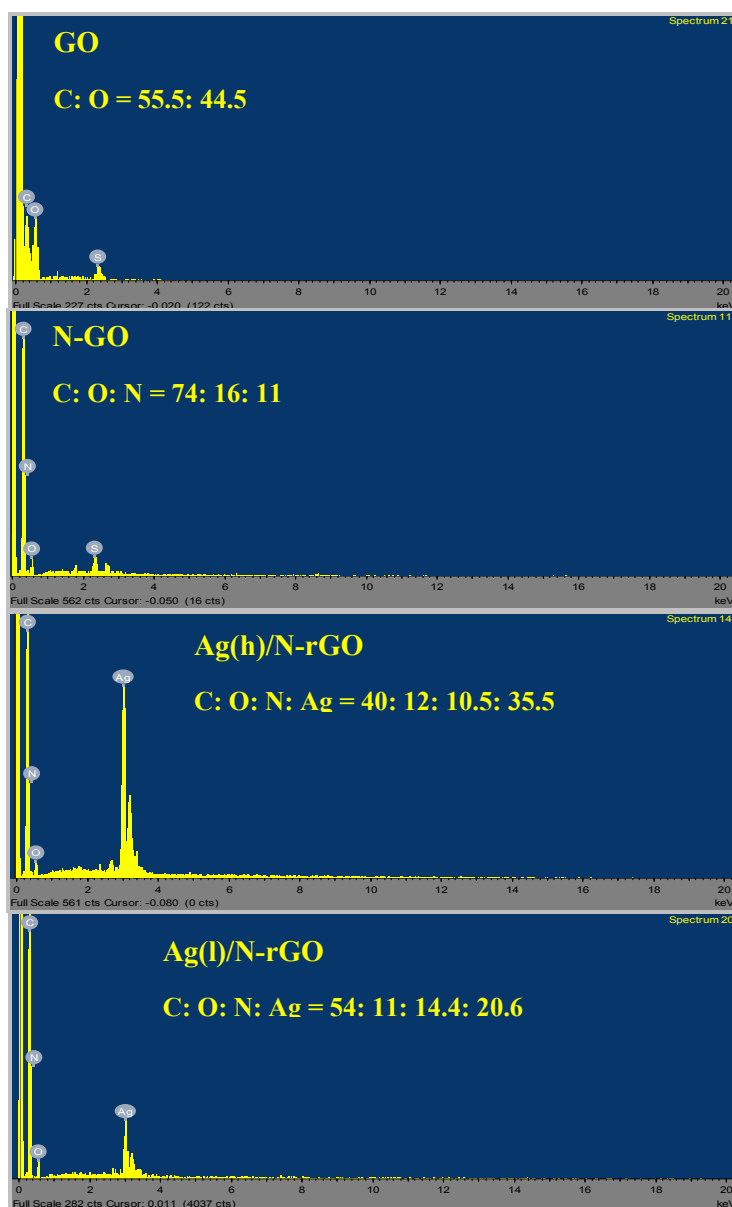


Fig 3. Shows the energy dispersive X-ray spectra (EDS) (a) GO (b) N-rGO (c) Ag(h)/N-rGO and (d) Ag(l)/N-rGO, respectively.

XPS analysis:

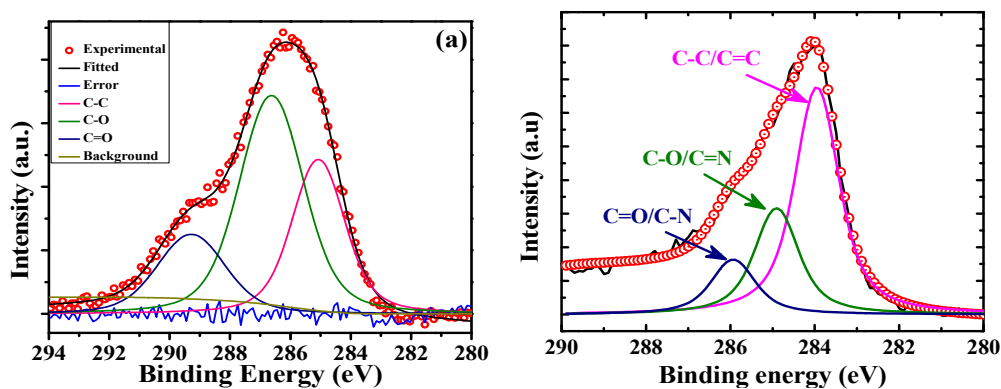


Fig.4 The XPS core level spectra of C1s (a) GO, (b) N-rGO.

ESI-4

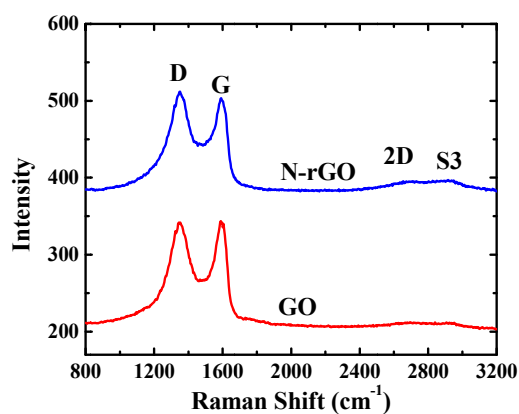
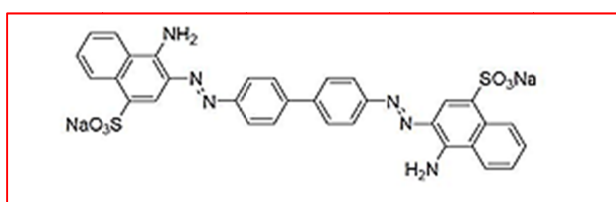
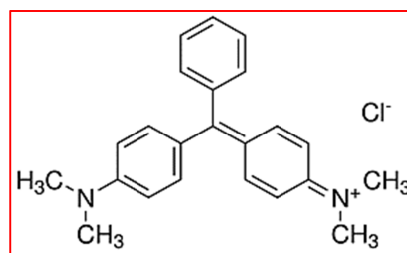


Fig 5. Represent the Raman spectroscopy of GO and N-rGO, respectively.

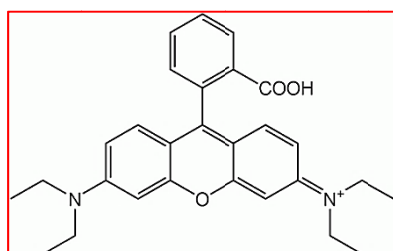
ESI-5



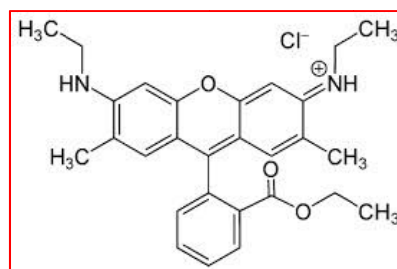
Congo red (CR)



Malachite Green (MG)



Rhodamine B (RhB)



Rhodamine 6G (Rh6G)

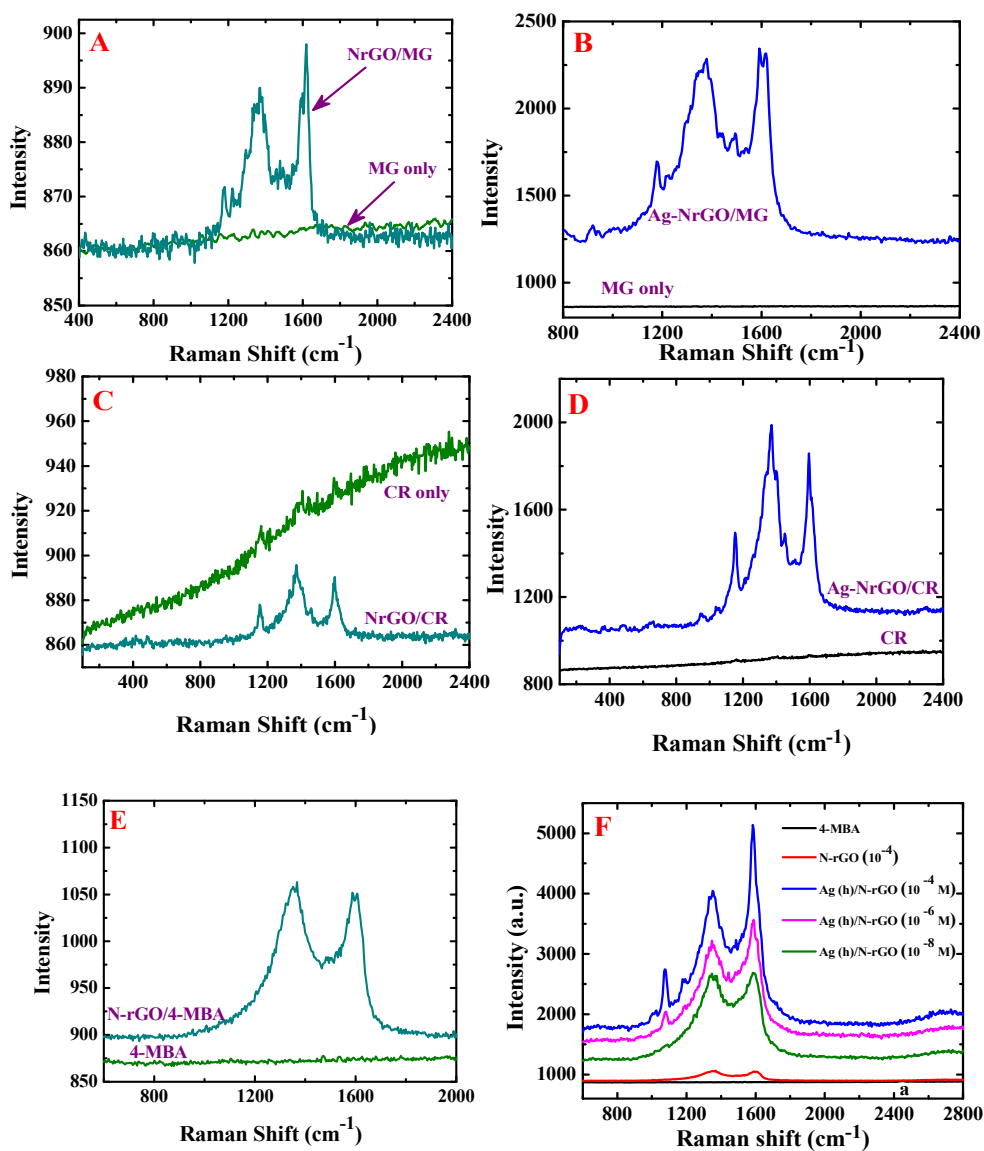


Fig.6 (A & B) Raman spectra of MG (100 μM), (C & D) CR (100 μM), and (E & F) 4-MBA in presence of N-rGO and Ag(h)/N-rGO substrate. The probe molecules are coated on soda lime glass substrate or N-rGO and Ag/N-rGO which are spread over the glass substrate. A Nd:YAG-532 nm laser is used to record the Raman spectra and integration time is 10 s for all the cases.

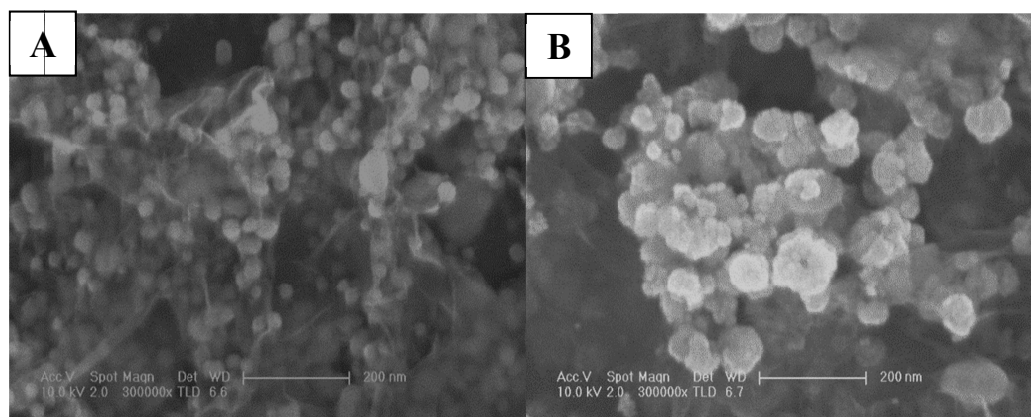


Fig.7 Shows the SEM images of Ag(h)/NrGO and (B) Pd/N-rGO, which is synthesized from this Ag(h)/N-rGO nanostructures, respectively.

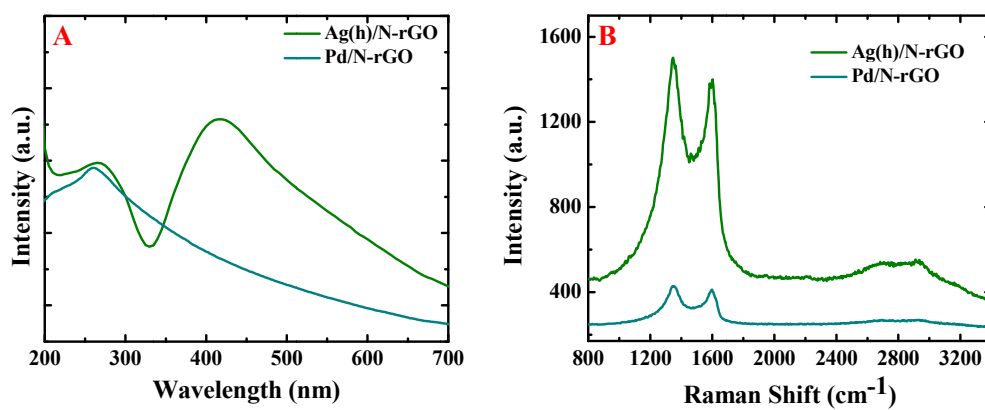


Fig. 8 Shows (A) UV-vis and (B) Raman spectra after the removal of Ag nanoparticles with the porous Pd by galvanic replacement reaction, respectively.